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LITHIUM SECONDARY BATTERY  
[Lichiumu niji denchi]

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[Claims]

[Claim 1] A lithium secondary battery having an anode, cathode, and lithium ion movable medium used for the absorption and release of lithium ions and as cathode active substances using intermetallic compounds of at least 1 or more kinds selected from the element group of Al, Ge, Pb, Si, Sn, and Zn and metals or semimetals from other than the element group.

[Claim 2] A lithium secondary battery according to Claim 1 wherein the intermetallic compounds which use cathode active substances have low crystallinity.

[Claim 3] A secondary battery according to Claim 1 wherein the intermetallic compounds which use cathode active substances are amorphous.

[Detailed Description of the Invention]

[0001] [Field of the Invention]

This invention relates to secondary batteries having an anode, cathode, and lithium ion movable medium with active substances that can absorb and release lithium.

[0002] [Prior Art]

Recently, electronic devices have become very small and light weight, and along with these striking developments has been the desire for small, lightweight high energy density batteries acting as power supplies. With primary batteries, small and light weight

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\* Paragraph numbers take place for the original pagination in the foreign text

batteries such as lithium batteries has been employed, but the application field for these devices has been limited. On the other hand, in the field of secondary batteries, lead and nickel-cadmium batteries have been conventionally used, but from the point of view of small size and light weight these batteries have been found lacking. From these perspectives, there has been a focus on non-aqueous electrolyte secondary batteries with an accumulation of research on non-aqueous electrolyte secondary batteries having lithium cathodes. These batteries have superior characteristics with high energy density, little self-discharge, and light weight. However, with these non-aqueous electrolyte secondary batteries, in keeping with advances in charge/discharge cycling, when charging and discharging, the lithium experiences crystal growth in the form of dendrites, making it highly probable that internal short-circuits would develop around the anode as defects, producing great damage during practical application.

[0003] Here, proposals have been made for non-aqueous electrolytes secondary batteries which use carbon material that have intercalated or doped lithium as cathode active material (below, called carbon cathode). In utilizing intercalation, graphite lamellar compounds are used as cathodes, for example, as disclosed in Patent JP S59-143280A. In addition, cathode materials have been built utilizing a doping phenomenon, having used carbon materials such as cured resins or cokes, as disclosed in Patents JP S58-35881A, JP S58-

209864A, JP S59-173979A, JP S62-90863A, JP S63-13282A, and JP H2-66856A. Actually, secondary batteries have been utilized with graphite or complex graphite carbon elements as cathode active material.

[0004] Moreover, it is made well-known to alloy a metal or semimetals, such as Al, Ge, Si, Sn, Zn, and Pb, with lithium, and the secondary batteries having cathode active substances which have alloyed these (below, called alloy cathodes) have been investigated. This kind of secondary battery has high capacity and high energy density and because it is capable of storing and releasing many more lithium ions than carbon cathodes, if comparing with carbon cathodes, it is possible to obtain high capacity and high energy density secondary batteries, but these types of batteries are not utilized because of their poor cycle characteristics.

[0005] Recently, attempts have been made at the development of secondary batteries that have higher capacity and longer cycle spans than those using carbon cathodes, with the indicated use, as cathode materials, iron silicide, nickel silicide, and manganese silicide (JP H5-159780A, JP H8-153517A, JP H8-153538A). In addition,  $\text{CaF}_2$  intermetallic compounds such as  $\text{Mg}_2\text{Ge}$  or  $\text{NiSi}_2$ , using as cathode materials, were identified at the 36<sup>th</sup> Battery Society Debate as having high capacity.

[0006] [Problems that the Invention is to Solve]

However, it is thought that progress in making high performance and light weight mobile electronic equipment will continue in the future, so that it is desirable to have high capacity, high energy density secondary batteries. Here, the invention's goal is to provide secondary batteries with the same capacity and energy density as those conventionally built using cathode active material with lithium or having metals or semimetals which have alloyed with lithium, and having cycle characteristics equivalent to secondary batteries which conventionally use carbon materials for the cathode active material.

[0007] [Means for Solving the Problem]

This invention solves the previously described problems. That is, this invention is a lithium secondary battery having an anode, cathode, and lithium ion movable medium used for the absorption and release of lithium ions and as cathode active substances using intermetallic compounds of at least 1 or more kinds selected from the element group of Al, Ge, Pb, Si, Sn, and Zn and metals or semimetals from other than the element group, wherein the intermetallic compounds which use cathode active substances have low crystallinity and wherein the intermetallic compounds which use cathode active substances are amorphous.

[0008] The cycle characteristics of the secondary battery of this invention are superior compared to secondary batteries which use conventional alloy cathodes, and, in addition, have superior capacity

and energy density compared to carbon cathodes. The reason for the advantages lies in that with alloy cathodes fine crystallization occurs of the active material when repeatedly charging and discharging, with pulverization seen, and using for this invention other elements which are difficult to alloy with lithium surrounding the original elements which alloyed with lithium such as Al, Ge, Si, Sn, Zn, and Pb, the fine crystallization and pulverization as described above is not observed. Other elements that prove difficult to alloy with lithium are, as examples, B, Co, Cr, Cu, Fe, Mn, Mo, Ni, Ti, V, and W.

[0009] In addition, it is more desirable to use low crystallinity or amorphous materials for the intermetallic compound used in this invention. Low crystallinity is defined, using X-ray diffraction employing CuK alpha rays, as having a half-value width at maximum peak strength of  $2\theta$ , less than  $0.6^\circ$ . In addition, here, referring to amorphous, again using X-ray diffraction employing CuK alpha rays, means a  $2\theta$  value with a broad dispersion band, having a peak from  $20^\circ$  to  $40^\circ$ , and may have a crystallinity peak. By using intermetallic compounds which are amorphous or have low crystallinity, because hardly any fine crystallization or pulverization of the active material occurs following repeated charging and discharging, it is possible to further improve cycling characteristics.

[0010] For the fundamental construction elements of the secondary battery of this invention, there has been mentioned cathode and anodes comprised of active material which can store and release lithium and lithium movable medium. More specifically, the following intermetallic compounds as cathode active materials used in the secondary battery of this invention are indicated, but there are no restrictions. As for those compounds containing Al: AlAs, Al<sub>2</sub>Au, AlAu<sub>2</sub>Mn, Al<sub>2</sub>Ca, Al<sub>2</sub>Ce, beta-AlCo, gamma'-AlCo<sub>3</sub>, AlCr<sub>2</sub>, theta-Al<sub>2</sub>Cu, AlCu<sub>2</sub>Mn, Al<sub>3</sub>Er, AlFe, AlFe<sub>3</sub>, Al<sub>3</sub>Ho, Al<sub>2</sub>La and Al<sub>3</sub>Mg<sub>4</sub>, Al<sub>8</sub>Mg<sub>5</sub>, AlMo<sub>3</sub>, AlNb<sub>3</sub>, AlNd, beta-AlNi, gamma'-AlNi<sub>3</sub>, AlNi<sub>2</sub>Ti, Al<sub>2</sub>Np, Al<sub>3</sub>Np, AlP, AlPd, Al<sub>2</sub>Pt, Al<sub>2</sub>Pu, AlSb, AlSc, AlTh<sub>2</sub>, Al<sub>2</sub>Th, Al<sub>2</sub>U, Al<sub>3</sub>U, Al<sub>2</sub>Y, Al<sub>3</sub>Yb, AlZr<sub>3</sub>, Al<sub>2</sub>Zr are mentioned.

[0011] As for Ge: As<sub>3</sub>GeLi<sub>5</sub>, CoFeGe, CoGeMn, FeGe<sub>2</sub>, Fe<sub>1.7</sub>Ge, FeGeMn, FeGeNi, GeLi<sub>5</sub>P<sub>3</sub>, GeMg<sub>2</sub>, GeMnNi, GeMo<sub>3</sub>, beta'-Ge<sub>2</sub>Mo, GeNb<sub>3</sub>, GeNi 1.70, GeNi<sub>3</sub> and Ge<sub>3</sub>Pu, Ge<sub>3</sub>U, GeV<sub>3</sub>, etc. are mentioned. As for those compounds containing Pb: AuPb<sub>2</sub> and Au<sub>2</sub>Pb, CaPb<sub>3</sub>, IrPb, KPb<sub>2</sub>, LaPb<sub>3</sub>, beta-LiPb, Mg<sub>2</sub>Pb, PbPd<sub>3</sub>, Pb<sub>2</sub>Pd, Pb<sub>2</sub>Pd<sub>3</sub>, Pb<sub>3</sub>Pr, PbPt, PbPu<sub>3</sub> and Pb<sub>2</sub>Rh, Pb<sub>3</sub>U, PbV<sub>3</sub>, etc. are mentioned. As for compounds containing Si: As<sub>3</sub>Li<sub>5</sub>Si, BeSiZr, CoSi<sub>2</sub>, beta-Cr 3Si, Cu<sub>3</sub>Mg<sub>2</sub>Si, Fe<sub>3</sub>Si, Li<sub>5</sub>P<sub>3</sub>Si, Mg<sub>2</sub>Si, MoSi<sub>2</sub>, Nb<sub>3</sub>Si, NiSi<sub>2</sub>, theta-Ni<sub>2</sub>Si, and beta-Ni<sub>3</sub>Si, ReSi<sub>2</sub>, alpha-RuSi, SiTa<sub>2</sub> and Si<sub>2</sub>Th, Si<sub>2</sub>U, beta-Si<sub>2</sub>U, Si<sub>3</sub>U, SiV<sub>3</sub>, Si<sub>2</sub>W, and SiZr<sub>2</sub>, etc. are mentioned.

[0012] As for compounds containing Sn, AsSn, AuSn, CaSn<sub>3</sub>, CeSn<sub>3</sub>, CoCu<sub>2</sub>Sn, Co<sub>2</sub>MnSn, CoNiSn, CoSn<sub>2</sub>, Co<sub>3</sub>Sn<sub>2</sub>, CrCu<sub>2</sub>Sn, Cu(Cr, Ni)<sub>2</sub>Sn, Cu<sub>2</sub>FeSn, CuMgSn, Cu<sub>2</sub>MnSn, Cu<sub>4</sub>MnSn, ItPdSn(s), (Cu, Ni)<sub>3</sub>Sn, Cu<sub>2</sub>NiSn, CuSn, FeSn<sub>2</sub>,



IrSn, IrSn<sub>2</sub>, LaSn<sub>3</sub>, MgNi<sub>2</sub>Sn, Mg<sub>2</sub>Sn, MnNi<sub>2</sub>Sn, MnSn<sub>2</sub>, Mn<sub>2</sub>Sn, Mo<sub>3</sub>Sn, Nb<sub>3</sub>Sn, NdSn<sub>3</sub>, NiSn, Ni<sub>3</sub>Sn<sub>2</sub>, Pd<sub>3</sub>Sn and Pd<sub>3</sub>Sn<sub>2</sub>, PrSn<sub>3</sub>, PtSn, PtSn<sub>2</sub>, Pt<sub>3</sub>Sn, PuSn<sub>3</sub>, RhSn, Rh<sub>3</sub>Sn<sub>2</sub>, RuSn<sub>2</sub>, SbSn, SnTi<sub>2</sub>, Sn<sub>3</sub>U, and SnV<sub>3</sub>, etc. are mentioned.

[0013] As for the compounds containing Zn: AgAsZn, beta-AgZn, AsLiZn, AsNaZn, beta-AuZn, CeZn, beta'-CuZn, EuZn, LaZn, LiPZn, MgNiZn, MgZn<sub>2</sub>, PrZn, and Pt<sub>3</sub>Zn, PuZn<sub>2</sub>, Th<sub>2</sub>Zn, TiZn<sub>2</sub>, TiZn<sub>3</sub>, Zn<sub>2</sub>Zr, etc. are mentioned. The formation of the intermetallic compounds which are used in the secondary battery of this invention, with fluorescent X-ray analysis of unaltered powder of the intermetallic compounds, can be equally determined by ICP analysis or electron absorption analysis of solutions which have dissolved the powder using concentrated hydrochloric acid, heat concentrated sulfuric acid, concentrated nitric acid, an aqua regia. In addition, other elements such as B or Co which are not in the formation of the previously described intermetallic compounds or other compounds may be present if present in amounts than 10 wt.%.

[0014] Under inert gas ambient atmospheres, such as an argon and nitrogen, the intermetallic compound used for the secondary battery of this invention is the powder or granular object which was carried out to specified quantity weighing capacity for each pure element, and was mixed, obtained by heating to more than the melting point, making it dissolve, and making it solidify after that in an electric furnace, high-frequency-induction-heating equipment, or an arc fusion furnace. In addition, it can also be obtained from each oxide by

using a reduction diffusion method. Moreover, melting of the crystalline intermetallic compound produced as mentioned above is carried out with high-frequency-induction-heating equipment, plasma jet equipment, infrared centralized heating apparatus, etc. and a well-known super-quenching method is used to give it low crystallinity or an amorphous nature. As a super-quenching method, the following methods can be used: gun method of ceramic processing pp. 218-219 (Gihodo Shuppan 1987), Hammer-Anvil method, slap method, the gas atomizing method, the water atomizing method, the disk type atomizing method, the plasma-spraying method, a centrifugal quenching method, the piece rolling method, the congruence rolling method, and melt drag. Especially, with a liquid chill roll method like the piece rolling method or the congruence rolling method, at  $10^5 - 10^6$  K/sec and the gas atomizing method, the cooling rate of  $10^4 - 10^5$  K/sec is obtained, and an amorphous intermetallic compound of this invention can be obtained easily. It is also possible to obtain a thin film-like amorphous substance intermetallic compound by the spatter method. Moreover, production of a low crystalline or amorphous intermetallic compound performs like a ball mill etc. with mechanical destruction for a crystalline intermetallic compound and it is possible also to mechanically alloy from each pure element.

[0015] The intermetallic compound which is embodied as the shape of the powder in the shape of the tabular ingot obtained by the above methods or as a globular shape, and a flake or a ribbon, is made into

the shape of impalpable powder by using well-known grinding, classification, and by mixed methods with particle size distribution adjusted. As mean particle diameter, it is desirable that the diameter be 1  $\mu\text{m}$  or more and 50  $\mu\text{m}$  or less. That by which the electrode binder layer was formed on the electrode charge collector is used for the electrode used for the secondary battery of this invention. With this kind of electrode the electrode collector is coated with an electrode combination slurry obtained from dispersing in a solvent the electrode combination which had mixed a binder with the intermetallic compounds, and as necessary, as conductor filler, afterwards drying. In addition, as necessary, the compound was roller pressed.

[0016] Although not limited especially as a charge collector used for the cathode of this invention, metal foil producing or in nets of thickness of about 10 - 100micro, such as Cu, nickel, and stainless steel, etc. are used. Although polytetrafluoroethylene, poly trifluoro ethylene, polyethylene, nitrile rubber, polybutadiene rubber, isobutylene-isoprene-rubber, polystyrene, styrene-butadiene-rubber, styrene butadiene latex, polysulfide rubber, nitrocellulose, acrylonitrile-butadiene rubber, and vinyl fluoride, polyvinylidene fluoride, a fluororubber, etc., are desirable as a binder, the binder is not restricted especially.

[0017] Moreover, when the electric resistance of an active material is high, in order to raise conductivity, an electric

conduction filler may be added. As an electric conduction filler, carbon materials, such as a graphite and carbon black, and metal powder, such as Cu, Fe, and Ti, are used. As an active material of the anode combined with the cathode of this invention, the lithium content metallic oxide expressed with the chemical composition type  $\text{Li}_x\text{M}_y\text{N}_z\text{O}_2$  (M expresses at least one kind chosen from cobalt, nickel, manganese, and other transition metals, N expresses at least one kind of non-transition metals, and x, y and z are  $0.05 < x < 1.10$ ,  $0.85 \leq y \leq 1.00$ , and  $0 \leq z < 0.10$  respectively) can be used. Potential is high, and a high voltage is obtained as a cell and these have good cyclic characteristics. As for M, it is especially desirable to have Co, Ni, Mn independently and Co/Ni, Mn/Cr, Mn/Fe as complexes. As for N, as long as the compounds are non-transition metal, there are no special restrictions, with Al, In, and Sn desirable. In addition, it is possible to use metal oxides expressed by  $\text{Li}_{(1+x)}\text{Mn}_{(2-x)}\text{O}_4$  ( $0 \leq x \leq 1$ ). When the cathode active material contains the lithium, it is also possible to use metallic oxides, such as metallic sulfide, such as  $\text{TiS}_2$ ,  $\text{TiS}_3$ ,  $\text{MoS}_3$ , and  $\text{FeS}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{V}_6\text{O}_{13}$ , and  $\text{MoO}_3$ .

[0018] Although about a 10-100-micrometer thickness metal foil or net, such as Al, Cu, Ni, and stainless steel, etc., can be used, when using an active material which has 4V potential like a lithium transition-metals oxide as a charge collector of an anode, it is desirable to use a metal foil or net made from Al. As a lithium ion medium for this invention, a solution which dissolved lithium salt in

aprotic organic solvent, for example, the solid-state which made the macromolecule matrix distribute lithium salt or the solution which dissolved lithium salt in an aprotic organic solvent are used. As for said organic solvent, it is desirable to use a straight chain carbonate, such as ethylene carbonate, dimethyl carbonate and diethyl carbonate, and ethyl methyl carbonate, as an indispensable component. In addition, ether, ketones, lactone, nitril, amines, amides, a sulfone system compound, carbonate, and ester may be used. As examples, although propylene carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyl lactone, a tetrahydrofuran, 1, 3-dioxolane, the 4-methyl -1, 3-dioxolane, diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, propionitrile, etc. are mentioned, it is not necessarily limited to these compounds. As for lithium salts,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{CF}_3\text{SO}_3\text{Li}$ ,  $\text{CH}_3\text{SO}_3\text{Li}$ ,  $\text{LiI}$  and  $\text{LiP}$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $2(\text{CF}_3\text{SO}_2)\text{NLi}$ , etc. are cited. Moreover, as macromolecular matrix, aliphatic series polyesters, such as aliphatic series polythioethers, such as aliphatic series polyethers, such as polyethylene oxide, polypropylene oxide, polytetramethylene oxide, polyvinyl alcohol, and a polyvinyl butyral, a polyethylene sulfide, and a polypropylene sulfide, polyethylene succinate, a polybutylene horse mackerel peat, and the poly caprolactone, polyethyleneimine, polyimide, polyvinylidene fluoride, its precursor, etc. can be used, for example.

[0019] Moreover, the separator for short circuit prevention can be formed between a anode and a negative electrode. As a separator, nonwoven fabrics, such as independent fine porosity film of polyolefines, such as polyethylene and polypropylene, or film which stuck them, and polyolefine, polyester, a polyamide, cellulose, are also independent, or the above-mentioned fine porosity film and the stuck film can be used.

[0020] As other components of the secondary battery of this invention, components, such as a terminal, an electric insulating plate, and a metal can may be used. Moreover, Figure 1 shows the invention used as a cell, employing stainless steel, nickel plating steel, iron, Al, etc. The structure of the cell is not especially limited to the shape of the cylinder shown in Figure 1, which rolled a paper type cell to make the anode, the cathode, and the separator as a monolayer, the laminating the cell of the anode, the cathode, and the separator in the shape of a roll, and other embodiments such as a square shape-like cell etc. are mentioned.

[0021] [Embodiments]

Hereafter, embodiments and comparative examples for this invention are explained in detail, though the scope of the invention is not limited to the embodiments.

[0022] [Embodiments] Embodiments 1-A - 1-N

Cathode active material,  $\text{AlFe}_3$  and  $\text{AlNi}_3$  of high crystallinity,  $\text{AlNi}_2\text{Ti}$ ,  $\text{Mg}_2\text{Pb}$ ,  $\text{PbV}_3$ ,  $\text{GeMg}_2$  and  $\text{GeNi}_3$ ,  $\text{Mg}_2\text{Si}$ ,  $\text{NiSi}_2$  and  $\text{SiV}_3$ ,  $\text{Mg}_2\text{Sn}$ ,

$\text{Cu}_2\text{NiSn}$ , and the example using  $\text{MgZn}_2$  and  $\text{TiZn}_2$  (considered as active material A-N respectively hereafter) are shown.

#### [0023] Preparation of High Crystallinity Intermetallic Compounds

After heat processing powder which mixed according to stoichiometry of each pure element of the active elements A-N using an electric furnace under an argon atmosphere, and after heat treating for approximately 2 hours at each of the temperatures shown in Table 1, cooling was done slowly, the material solidified giving a plate-shaped intermetallic compound. The coarse powder obtained by pulverizing this plate-shaped material was made into particles by a sample mill, and by screening with a 400 mesh, fine particles of uniform diameter 9  $\mu\text{m}$  were obtained.

#### [0024] X-ray Diffraction

For the active material F as a representative example, Fig. 2 shows the measured results of X-ray diffraction using  $\text{CuK}$  alpha rays. This ray use showed the high crystallinity of the intermetallic compounds, with a first strong peak of diffraction intensity near  $24.2^\circ$ , and the half value width of this peak was  $0.16^\circ$ . High crystallinity was confirmed for other active materials in the same way.

#### [0025] Composition Analysis

Every active material's composition was confirmed with composition analysis by ICP analysis of aqueous solutions which dissolved the intermetallic compounds in aqua regia.

## Cathode Preparation

Mix 42 wt. % of the intermetallic compound prepared as before, 4 wt. % of the graphite fragments (Lonza (company) KS6) as conductive filler, 2 wt. % of acetylene black (Denki Kagu Denka Black), 36 wt. % of polyvinylidene solution as binder (after dissolving Kureha KF polymer-#9131 using 13 wt. % fixing rate for N-methyl-2-pyrrolidone, below PVdF solution) and 16 wt. % of N-methyl-2-pyrrolidone (below, NMP), and after stirring obtain an electrode combination slurry. After coating this slurry on top of copper foil 12  $\mu\text{m}$  thick which is the collector, and drying, roll press at 150  $^{\circ}\text{C}$ , to obtain a cathode of film thickness approximately 30  $\mu\text{m}$  which comprises the cathode collector and the cathode combination layer.

## [0026] Anode Preparation

To  $\text{LiCoO}_2$  100 weight parts with a production mean particle diameter of 3  $\mu\text{m}$ , a dimethylformamide solution (5 % of the weight) 100 weight parts which dissolved the graphite 5 weight part as an electric conduction agent, and dissolved polyvinylidene fluoride as a binder was added, mixed and stirred and the slurry was obtained. The anode which consists of a charge collector and an anode binder layer was produced by carrying out press forming of this slurry after coating and desiccation on an Al foil of 15-micrometer thickness.



#### [0027] Charge-Discharge Evaluation

In order to see the charge-and-discharge evaluation of cathode independence, cathode potential was controlled as follows and a cycle evaluation was performed. About the anode and negative electrode which were obtained as mentioned above, there was piercing to  $2.05\text{cm}^2$  with  $2.00\text{cm}^2$  respectively, and they were made to face each other through a fine porosity film made from polyethylene, and each electrode which welded the charge collector was put with a glass plate and a clip. After inserting into the alligator clip of a glass trial cell so that the charge collector of the anode and the negative electrode may not be short-circuited, the lithium metal which is a reference pole as it comes near the negative electrode was set. After, dissolving ethylene carbonate and methylethyl carbonate at a volume rate after decompressing the interior of this glass trial cell and removing enough moisture, and dissolving an electrolyte  $\text{LiPF}_6$  in the mixed solvent at 1:2, it was dehydrated by molecular sieves, and liquid was dropped at said glass trial cell which removed enough moisture under super-low humidity conditions, and the electrolytic solution was sufficiently infiltrated.

[0028] Thus, the charge and discharge test of the obtained trial cell was performed by controlling the potential of the cathode seen from the reference pole. Charge here is a direction where a negative electrode carries out occlusion of the lithium ion, and conversely, discharge is a direction which emits a lithium ion. In addition,

positive active material should cover the amount of lithium ion occlusion of a cathode with a just sufficient amount applied. Charge performed current density 1 mA/cm<sup>2</sup>, 10mV, and 24-hour constant-potential charge, and discharge performed 1.2V constant current cut-off discharge of current density 1 mA/cm<sup>2</sup>. The maintenance factor (henceforth, capacity maintenance factor) of the discharge capacity of the 100<sup>th</sup> cycle when making the amount of discharge per unit volume of the cathode binder layer of 1<sup>st</sup> cycle (henceforth, discharge capacity), and discharge capacity of 1<sup>st</sup> cycle as 100% from the binder layer volume of this cathode was used.

[0029] Comparative Examples 1-O-1-T

Examples are shown using Al, Ge, Pb, Si, Sn, and Zn as alloy cathodes. Powder was procured from high purity chemical research laboratory preparations from each metal or semimetal, and fine powder was used obtained by screening with 400 meshes. Beyond these new procedures, the experimentation and evaluation was done in the same way as with embodiments 1-A-1-N.

[0030] Comparative Examples 1-U, V

The examples used scale-like graphite (CX3000 by Chuetsu Graphite Works Co., Ltd. Co., Ltd., following graphite) and needle coke (Okikazu Petroleum company, following cokes) as a carbon cathode. A mixture was obtained by adding 47 wt. % of each carbon material, 36 wt. % of PVdF solution, and 17 wt. % of NMP and after stirring gave an electrode combination slurry that was the cathode, with

experimentation and evaluation done in the same way as with  
embodiments 1-A-1-N.

[0032] [Table 1]

a 高結晶性金属間化合物					b 低結晶性又は非晶質な金属間化合物				
RunNo.	c 作製方法	d 電容量 Ah/cm <sup>3</sup>	e サイクル性 %		RunNo.	c 作製方法	d 電容量 Ah/cm <sup>3</sup>	e サイクル性 %	
AlFe <sub>2</sub>	実施例 1-A	電気炉 (800°C)	758	51	実施例 3-A'	RS法	763	87	
AlNi <sub>2</sub>	実施例 1-B	電気炉 (800°C)	723	52	実施例 2-B'	MA法	732	79	
AlNi <sub>2</sub> Ti	実施例 1-C	電気炉 (1700°C)	725	60	実施例 3-C'	RS法	740	90	
Mg <sub>2</sub> Pb	実施例 1-D	電気炉 (700°C)	570	55	実施例 2-D'	MA法	575	75	
PbV <sub>3</sub>	実施例 1-E	電気炉 (1500°C)	565	53	実施例 3-E'	RS法	571	86	
CoNi <sub>2</sub>	実施例 1-F	電気炉 (850°C)	1883	51	実施例 2-F'	MA法	1884	72	
CoNi <sub>2</sub>	実施例 1-G	電気炉 (1500°C)	1010	49	実施例 3-G'	RS法	1013	90	
Mg <sub>2</sub> Si	実施例 1-H	電気炉 (850°C)	1015	53	実施例 2-H'	MA法	1101	74	
NiSi <sub>2</sub>	実施例 1-I	電気炉 (1500°C)	1437	65	実施例 3-I'	RS法	1450	91	
SiV <sub>3</sub>	実施例 1-J	電気炉 (1850°C)	870	52	実施例 3-J'	RS法	874	88	
Mg <sub>2</sub> Sn	実施例 1-K	電気炉 (700°C)	1073	60	実施例 2-K'	MA法	1080	81	
Cu <sub>2</sub> NiSn	実施例 1-L	電気炉 (1500°C)	911	65	実施例 3-L'	RS法	915	92	
MgZn <sub>2</sub>	実施例 1-M	電気炉 (700°C)	813	47	実施例 2-M'	MA法	820	74	
TiZn <sub>2</sub>	実施例 1-N	電気炉 (1000°C)	791	51	実施例 3-N'	RS法	801	89	
Al	比較例 1-O	市販	1220	20					
Pb	比較例 1-P	市販	2354	23					
Ge	比較例 1-Q	市販	3250	27					
Si	比較例 1-R	市販	3991	31					
Sn	比較例 1-S	市販	3145	35					
Zn	比較例 1-T	市販	2245	24					
炭粉	比較例 1-U	市販	380	97					
コークス	比較例 1-V	市販	300	95					

Key:

- a) High crystallinity intermetallic compounds;
- b) Low crystallinity or amorphous intermetallic compounds;
- c) Preparation method;
- d) Discharge capacity;
- e) Cycle;
- f) Embodiment;
- g) Comparative;
- h) Electric furnace;
- i) Commercial;
- j) method;
- k) Graphite;
- l) Coke.

[0033] Thus, in this way, it is understood that for the cathode  
which uses for its active material intermetallic compounds containing  
Al, Ge, Pb, Si, Sn, and Zn of embodiments 1-A-1-N has very high

discharge capacity compared to carbon cathodes, and in addition, has superior cycle properties compared to alloy cathodes.

Embodiments 2-B', D', F', H', K', and M'

Examples are shown which use  $\text{AlNi}_3$ ,  $\text{Mg}_2\text{Pb}$ ,  $\text{GeMg}_2$ ,  $\text{Mg}_2\text{Si}$ ,  $\text{Mg}_2\text{Sn}$ , and  $\text{MgZn}_2$  (below, use B', D', F', H', K, and M' for each active material) of low crystallinity as the cathode's active material.

#### [0034] Low crystallinity intermetallic compound preparations

In order to obtain a low crystallinity intermetallic compound, use the manufacturing method called mechanical alloying (MA method). When explaining concretely this MA method, there is entered 5g of powder that was mixed in stoichmetric ratios for every element of the active materials B', D', F', H', K, and M' in an argon atmosphere in a stainless stell pot mill of internal capacity 500 cm<sup>3</sup> along with 8 stainless steel balls of diameter 25mm, with the rotating ball mill operating for 2 weeks. By screening using 400 mesh the powder that was obtained after processing with the ball mills, fine powder was obtained of uniform particle diameter 9  $\mu\text{m}$ . As a representative example, consider the active substance F', with Fig. 3 showing the measurement results of X-ray diffraction using CuK alpha rays. The measurements shows a intermetallic compound of low crystallinity, with the first strong peak at a diffraction angle of 24.1°, and the half value width at this peak of 0.66°. Also with other active materials, low crystallinity was confirmed in the same way. The

evaluations of subsequent experiments used the same method as with embodiments 1-A-1-N.

[0035] (Embodiments 3-A', C', E', G', I', J', L', and N')

As the cathode active material, an example was shown using amorphous  $\text{AlFe}_3$ ,  $\text{AlNi}_2\text{Ti}$ ,  $\text{PbV}_3$ ,  $\text{GeNi}_3$ ,  $\text{NiSi}_2$ ,  $\text{SiV}_3$ ,  $\text{Cu}_2\text{NiSn}$ ,  $\text{TiZn}_2$  (below, called A', C', E', G', I', J', L', and N')

#### Amorphous intermetallic compound preparation

In order to obtain an amorphous intermetallic compound, a high frequency induction heating and super quenching device was used (below RS method). The high frequency source using a transistor inverter method, had power of 3KW at a frequency of 200KHz. The fragment roller was copper, with dimension diameter 200mm and width 20mm, and in addition, the roller drive method was magnetic coupling, rotating at 3000rpm. Using the RS method on 10g of each high crystallinity intermetallic compound which was manufactured by the same method indicated in embodiments 1-A-1-N, the material was then super quenched in an argon atmosphere to obtain a ribbon-shaped material. By using a sample mill on the ribbon-shaped material, powder was obtained, and by screening with 400 mesh, uniform particles of diameter 9  $\mu\text{m}$  were obtained for the active materials A', C', E', G', I', J', L', and N'. The amorphous nature of the materials was confirmed using X-ray diffraction measurements using CuK alpha rays. Subsequent experiments and evaluations were performed using the

same methods as for embodiments 1-A-1-N. The results are shown in Table 1.

[0036] Cathode materials were used of low crystallinity of amorphous intermetallic compounds containing the Al, Ge, Pb, Si, Sn, and Zn of Embodiments 2 and 3, and large capacity retention was high compared to the use of high crystallinity intermetallic compounds of Embodiment 1, and it was understood that the cycle properties were superior.

[0037] [Effect of the Invention]

The cathode which used the intermetallic compound containing Al, Ge, Pb, Si, Sn, and Zn for its active material has a high discharge capacity compared with a carbon cathode, and the cycle properties are excellent compared with the alloy cathode. Therefore, the secondary batteries of this invention have high capacity and a high energy consistency far greater than present secondary batteries which use the carbon anode, and have the cycle properties better than the secondary batteries using an alloy cathode. Moreover, better cycle properties can be acquired by using a low crystalline or amorphous intermetallic compound for a cathode's active material.

[Brief Description of the Drawings]

[Figure 1] It is the schematic diagram showing an embodiment of the nonaqueous electrolyte secondary battery of this invention.

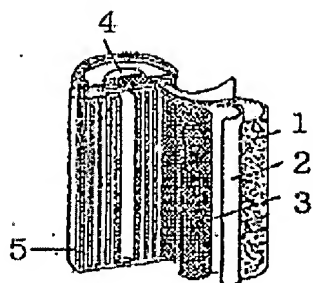
[Figure 2] It is the results of the X diffraction of the high crystallinity intermetallic compound  $\text{GeMg}_2$ .

[Figure 3] It is the results of the X diffraction of the low crystallinity intermetallic compound  $\text{GeMg}_2$ .

[Explanation of the Elements]

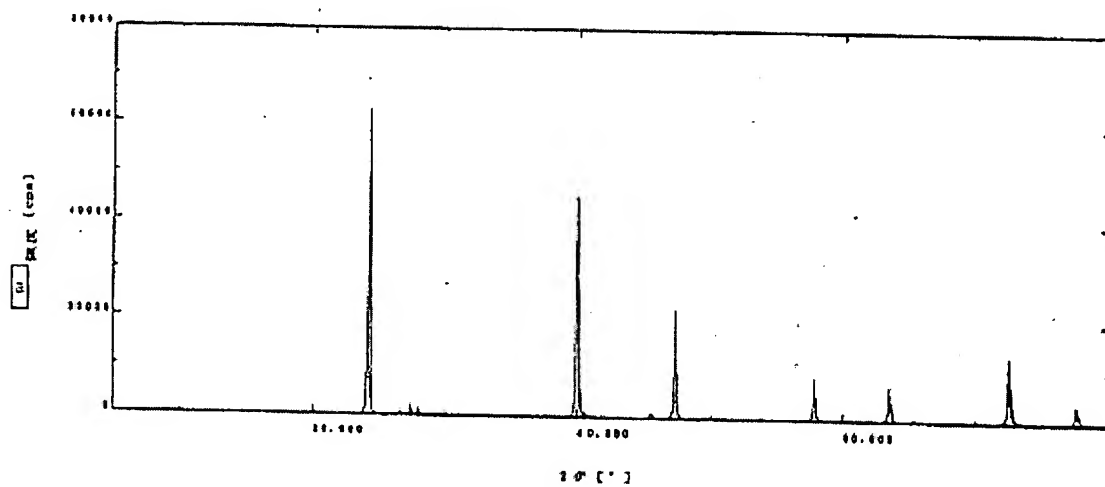
- 1 -- Cathode
- 2 -- Separator
- 3 -- Anode
- 4 -- Anode terminal
- 5 -- Cell container (cathode terminal)

Figure 1



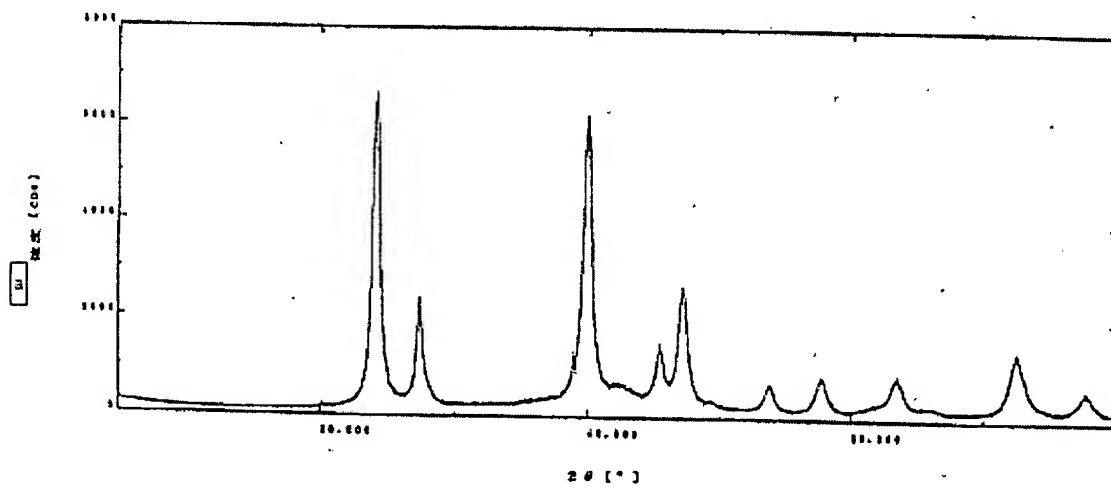
/8

Figure 2



Key: a) Intensity.

Figure 3



Key: a) Intensity.